I. THE EXTENSION OF IMPROVED X-RAY DIFFRACTION METHODS TO PREVIOUSLY UNINVESTIGATED TYPES OF ORGANIC COMPOUNDS WITH GENERALIZATIONS ON SPACE GROUP PREFERENCES.

II. CORRELATION OF THERMAL AND STRUCTURAL ANALYSES APPLIED TO DOLOMITIC LIME REACTIONS.

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Part I

The Extension of Improved X-ray Diffraction Methods to Previously Uninvestigated Types of Organic Compounds with Generalizations on Space Group Preferences.

Introduction

In order to facilitate the study of the X-ray crystallography of organic compounds, a critical survey of 315 typical organic compounds (gathered from the Strukturbericht)[1] was undertaken. This was required, since no similar survey exists.

This study disclosed some very striking results. For example, 67.9% of the crystals studied belonged to the monoclinic system, 12.1% to the orthorhombic system and the remainder to the other five crystal systems. Further, 58.7% of the substances fell into only three space groups.

The subject of space group for optically active organic compounds is given special consideration, in terms of theory and practical use in prediction. The most important consideration is the aid of the limitation to one of the eleven enantiomorphous point groups. The observation of the tremendous preponderance of the space group P 2_1 among optically active organic compounds crystallizing in the monoclinic system, provides a useful point of departure for the study of many sugars and alkaloids.

Experimental Results

Rotation patterns and Weissenberg patterns[2] provided the evidence for indexing the X-ray interferences. For accurate measurements of unit cell parameters powder patterns made in new cameras of high precision were employed.

The study includes ten organic compounds upon which no previous X-ray data could be found. Three of these materials were optically active. In each case a unit cell and probable space group are assigned, as follows:

Compound	Crystal System	a	b	c	β or γ	Space Group	
1. Cinchonidine	Orthorhombic	21.0Å	10.6Å	7.12Å		$P2_12_12_1$	(1)
2. Lactose	Monoclinic	22.0	7.80	4.85	109°.8	$P2_1$	(2)
3. Lactose . H_2O	"	13.3	11.4	4.92	92°	$P2_1$	(3)
4. P - Urazine	"	11.4	5.18	8.30	93°	Cc or C 2/c	(4)
5. Phenoxyacetic Acid	"	12.4	11.4	5.28	94°	$P2_1/c$	(5)
6. 4 Methyl-Phenoxyacetic Acid	"	14.0	12.0	5.16	110°	$P2_1/c$	(6)
7. Phenthioacetic Acid	"	18.8	7.50	6.15	108°	$P2_1/m$	(7)
8. 4-Methyl-Phenthioacetic Acid	"	29.2	5.94	5.64	103°	$P2_1/m$	(8)
9. Coumarin	Orthorhombic	15.6	7.75	5.60	.....	Pcc	(9)
10. Thiocoumarin	"	8.8	9.90	4.10	.....	Pcc	(10)

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1. Primitive cell, three twofold screw axis $(Z = 4)$.
2. Primitive cell, one twofold screw axis $(Z = 2)$.
3. $(Z = 2)$.
4. Face centered cell with a glide reflection plane or twofold axis perpendicular to glide reflection plane $(Z = 4)$.
5. Primitive cell, one twofold screw axis perpendicular to glide reflection plane $(Z = 4)$
6. $(Z = 4)$
7. Primitive cell, one twofold screw axis perpendicular to mirror plane $(Z = 4)$
8. $(Z = 4)$
9. Primitive cell with two glide reflection planes $(Z = 2)$.
10. $(Z = 2)$

Part II

Correlation of Thermal and Structural Analyses Applied to Dolomitic Lime Reactions.

Introduction

In continuation of researches on lime problems under the auspices of the National Lime Association ,[3] certain controversial problems of particular difficulty and fundamental importance have been selected as requiring for their solution the application of new instrumental methods, particularly X-ray diffraction, electron microscopy, and thermal analysis.

It was particularly desired to investigate critically the claims of Dr. Wells and his group at the National Bureau of Standards that the failures of plasters made from dolomitic lime (containing unhydrated magnesia) were due in general to the hydration and carbonation of the magnesia.

A second phase of the lime work concerned the determination of the particle size of magnesia samples for use in the rubber industry, and also as a catalyst. This was accomplished by use of the breadth of interferences in powder patterns of the samples in question. A simple derivation of a formula for this purpose has been developed by Sir W. L. Bragg.[4]

Experimental Results

An X-ray diffraction study of various plasters from cases of plaster failures at the Detroit Leland Building, A.I.U. Citadel Building, Michigan Theatre, and a Chicago convent, was conducted. These diffraction patterns were examined carefully for $Mg(OH)_2$, $MgCO_3$, $MgCO_3.3H_2O$, but in no case could the hydroxide or carbonate be found. A final comparison of the films with one from a dolomitic plaster in the Pittsburgh County Court House (this plaster had been in service for seventy years without failure) failed to disclose any difference in the detected components.

To further study, and if possible confirm the previous data, recourse was taken to the thermal analyses of the plasters in question. The method had not been used previously for such samples. The thermal curves for more than 40 samples were made on the equipment of the Illinois Geological Survey through the cooperation of Dr. R. E. Grim, who has described the apparatus and technique in prior publications.[5] This study showed the presence of a small amount of $Mg(OH)_2$ on all the plasters which was not found in the X-ray work. No magnesium carbonate was found in either case.

In addition to the plaster, synthetic samples which had been subjected to treatment by both wet and dry CO_2 were studied. These consisted of samples of MgO, $Mg(OH)_2$, $Ca(OH)_2$ and Micro-Mag ($MgO\text{-}Ca(OH)_2$ in equimolar amounts). There was no action in the case of MgO or $Mg(OH)_2$ with either wet or dry CO_2. The other samples were carbonated by either wet or dry CO_2 with the formation of $CaCO_3$ alone.

From the work it was concluded that the failure of these dolomitic plasters was not due to the hydration and/or carbonation of the MgO contained. In many cases the failure seemed to be due to poor bonding to the wall or mechanical and thermal stresses. These conclusions are in direct opposition to the studies made by Dr. L. Wells and his group at the National Bureau of Standards. It, none the less, represents the study of many plaster failures by X-ray diffraction technique and the study and interpretation of forty-two separate samples by thermal analyses.

Particle size of twelve magnesia samples were obtained by use of the equation:

$$\frac{B}{R} = \frac{0.94 \cdot \lambda}{D \operatorname{Cos} (X/2)} + b$$

In this expression B is the breadth of the diffraction interference at points of half-maximum intesity. R is the radius of the camera measured in the same units as B; λ is the wave length of the radiation used. X is the angle of diffraction for the inter-

ference in question. D is the diameter of the particle in the same unit as λ. Finally, b is the minimum interference breadth in radians. The value of b was obtained graphically,[6] and values of D for each sample could be calculated. All samples, but one, were about 150 Å in breadth. The exception was about 300 Å.

Electron microscope pictures of all of the samples were taken with the cooperation of Dr. M. B. Baylor. These pictures indicated that the materials existed as aggregates of the primary particles.

By means of these micrographs it was possible to make a clear distinction between primary particle size evaluated from X-ray patterns and secondary aggregates. Only in this way is an explanation of catalytic action, measured by decomposition of hydrogen peroxide, and surface activity possible. Samples of French and German magnesias used for war-time purposes have been critically compared by these methods.

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Vita

The author was born at Metropolis, Illinois, December 17, 1924. He received his primary education in the Metropolis Public Schools. He received his secondary education at University High School, Urbana, Illinois, from where he graduated in June, 1941. He entered the University of Illinois in September, 1941, and studied in the chemistry curriculum. The degree of Bachelor of Science in Chemistry (with Honors) was received in February, 1944, and the degree of Master of Science in February, 1945.

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His publication is:

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